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FORMATION OF GLASS SYNTHESIZED BY SOL–GEL TECHNOLOGY

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The process of glass synthesis by the sol–gel method is studied using analysis of EPR spectra. The gelation process and formation of xerogels are considered depending on the temperature–time parameters and the type of initial components. It is established that the glass phase starts to be formed at 800°C.

The expanded use of glass in developing a new generation of instruments requires high-quality homogeneous glass materials. The improvement of all stages of glass production, including the melting process, is of great importance.

A promising method for producing homogeneous glasses is the sol–gel method.

Analysis of published sources suggests two directions in the technology of sol–gel synthesis of glasses.

Production of amorphous batches from gels and their subsequent melting according to the traditional technology. This direction is mainly focused on the synthesis of extra pure multicomponent glasses, primarily optical glasses, including glass for fiber optics. This technology includes preparation of solutions based on extra pure soluble materials (salts, metal hydroxides, organometallic compounds, SiO₂ sol), transition from the solution to a sol, then to a gel, its drying, and formation of an amorphous powder batch achieving a perfect (at the molecular level) mixing of the components [1].

Apart from the high purity and homogeneity of the glass, the use of such batch decreased (by 150–200°C) the vitrification temperature due to the high dispersion of the batch particles, its amorphous nature, and the emergence of chemical bonds typical of glass. At the same time, the high gas-saturation of the batch complicates the clarification process and in the case of high-viscosity melts sometimes prevents lowering the general melting temperature.

Production of glass by polycondensation (polymerization) of gel and its subsequent consolidation under heat treatment (without melting), i.e., the method implementing a gradual sol → gel → glass transition.

The purpose of our study is the investigation of sol–gel synthesis of alkali-free aluminocalcium silicate glass and stage-by-stage analysis of the structure of resulting materials depending on their temperature–time parameters and the type of initial material.

In the traditional technology such glass is melted in tank furnaces at 1560°C, the clarification temperature is 1520°C, and the working temperature 1450°C. The annealed samples contain bubbles and plenty of “fly-like” defects.

One can single out the following stages in sol–gel technology [2–4]:

- preparing solutions by mixing alkoxides or salts of the elements comprising glass with water and alcohol at a certain pH level and temperature;
- primary structurization of the solution, which is defined in [5] as complex formation; sol formation occurs at this stage [4, 6];
- gel formation, i.e., the formation of a 3D lattice as a result of hydrolysis and polycondensation reactions; a gel is formed from the solution and its structure determines subsequent processes; the processes of complex formation, hydrolysis, and polycondensation are simultaneous; with mutual overlapping, their duration depends on several factors and may vary within wide limits [5, 7];
- gel aging: the polycondensation reactions continue in the gel-like state, which is accompanied by a change in the gel structure, its decreasing porosity, and increasing strength;
- gel drying: the removal of the residual liquid phase consisting of mixed water, alcohol, and ethers from the gel pores; the structure of the gel changes with dehydration: from a soft jelly-like mixture it gradually transforms into a solid substance; dry gel is called xerogel.
- high-temperature treatment of xerogel to obtain a material in the form of glass.

The above parameters influencing the kinetics of gel and xerogel formation are adjusted in each particular case for the synthesis of multicomponent compositions and make it possible to obtain materials with preset service parameters.

To introduce SiO in the solution, we used tetraethyl orthosilicate (TEOS) Si(OC₂H₅)₄. The matrix elements were introduced via salts soluble in water and ethanol (nitrates, chlorides, acetates). In some cases oxides or carbonates of the elements were dissolved in concentrated nitric or hydro-

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chloric acid and then the solution of the nitrates or chlorides were used in synthesis. The solvents were bidistilled water and ethyl alcohol (absolute or 96% aqueous alcohol).

One of the main requirements imposed on all initial materials is a high degree of purity, especially regarding the content of heavy metals, which should not exceed $10^{-3}\%$. To prepare the main experimental series we used reactants of grades at least “analytically pure” and “chemically pure.”

Testing of solutions was performed in isothermal conditions at a temperature of $60 - 80^\circ\text{C}$ in a SNOL-3.5 drying cabinet or in a liquid thermostat with an agitator designed by the MOSZ GIS Institute that automatically maintains a preset temperature with an accuracy up to $\pm 0.05^\circ\text{C}$.

The obtained gels were dried in a SNOL-3.5 drying cabinet. The resultant materials were calcined in a muffle electric furnace at $300 - 850^\circ\text{C}$ under different exposures to produce xerogels. After that, melting was conducted in an electric furnace with Silit heaters to produce glass melt. Preference was given to quartz crucibles to avoid the migration of impurity cations into the glass melt, in particular, titanium ions from corundum crucibles.

The spectroscopy of electron paramagnetic resonance (EPR) is a method enabling one to study point paramagnetic centers that have their own magnetic momentum. These centers in glass can be defects, such as ruptured bonds, oxygen vacancies, and free radicals, as well as metal ions of the transition groups of the periodic system of elements. They are deliberately introduced or generated by ionizing radiation and used as glass structure indicators, since they give important information on the physical and chemical properties of materials.

One of the most convenient indicator ions for studying the glass structure is Cu^{2+} , which provides spectra in a wide temperature interval, has an anisotropic superfine structure (SFS), and is highly sensitive to the nearest environment of the ion. Accordingly, 5 wt.% CuO was introduced into the solutions.

EPR was measured on a RE-1306 modified radiospectrometer at 77 K and at room temperature. To determine EPR spectra parameters, they were compared with the spectra calculated on a computer using a program developed at the Nuclear Physics Institute of the Moscow State University.

The Cu^{2+} spectra were simulated using a computer. The spectral parameters of Cu^{2+} were determined by matching experimental spectra with the computer-calculated spectra. The EPR spectra were calculated assuming that they are described by an axial-symmetry spin hamiltonian with electron spin $S = 1/2$ and nuclear spin $I = 3/2$:

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y),$$

where β is the Bohr magneton; S_i are the electron spin components; I_i are the nucleus spin components; g_{\parallel} is the g factor where the magnetic field is oriented parallel to the longer axis of the copper complex; g_{\perp} is the g factor where the magnetic field is oriented along the perpendicular axes of the

complex that lie in the equatorial plane; A_{\parallel} and A_{\perp} are the STS constants for the parallel and perpendicular orientations of the external magnetic field.

A model spectrum was calculated in the form of the first derivative of the EPR absorption signal:

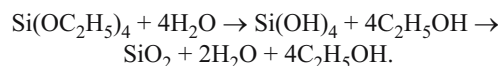
$$S'(H) = \sum_{m_i=3/2}^{m_i=3/2} \int_0^{\pi/2} W(\theta) F'_{m_i}(\theta, H) \sin \theta d\theta,$$

where $W(\theta)$ is the transformation probability depending on the orientation; F'_{m_i} are the first derivatives of individual absorption lines; the calculation was carried out with the variation interval of the angle θ equal to 1° .

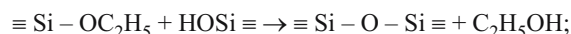
We chose the process of oxygen hydrolysis of TEOS, since the main hydrolysis can be performed only using ammonia or other basic nitrous components, such as triethanolamine $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$. Since glass contains cations Zn^{2+} , we observed a high propensity for the formation of complexes and their subsequent migration into the porous gel structure, as well as the probability of the complex migration to the liquid phase in syneresis, which inevitably impairs the product homogeneity. For the same reason we cannot use “ammonia rinsing” of the xerogel at the initial stages of drying and heat treatment to remove organic residues from the xerogel structure.

The sources of cations were the corresponding chlorides. The positive aspect of their use is their high solubility in water, which ensures a high gelation rate and a more concentrated product. This also facilitates the drying process and decreases the power consumption of the process, since its essential component is the heat capacity of hydrogel and the heat of evaporation of water and organic components.

The hydrolysis of TEOS proceeds according to the following scheme:



Polycondensation starts simultaneously with hydrolysis. Immediately after the formation of silanol groups ($\equiv \text{SiOH}$) the latter start reacting with ethoxy groups and form siloxane bonds $\equiv \text{Si} - \text{O} - \text{Si} \equiv$, i.e., polymerization takes place (the reactions below are simplified):



The reaction products, i.e., ethanol and water, participate anew in hydrolysis; linear polymers are formed in an acid medium and branched clusters in a basic medium. These reactions lead to the formation of round siliceous particles in the sol, and their subsequent coagulation results in gel formation.

The interaction of the hydrolysis and polycondensation processes is a characteristic feature of silicate systems, which

prevents precise registering the sol \rightarrow gel transformation. This transformation in aqueous-alcohol TEOS solutions is determined experimentally when the solution flow stops.

The duration of gel formation grows linearly with increasing ethanol/TEOS ratio, i.e., as the solution gets diluted. However, there is an optimum water/TEOS ratio ensuring a minimal gelation duration, and this ratio grows with increasing ethanol content.

The solution was intensely stirred with a magnetic agitator at a temperature of 60°C in a fluoroplastic vessel with a lid and a reverse chiller. Gelation lasted 24 h. The obtained gel was dried for 3 h in a thin layer at 70°C and then for 2 h in a muffle furnace at 100°C, then heated to about 400°C for 1 h and then to about 800°C in a crucible with a lid. A crystalline tarnish was observed on the lid, whose qualitative analysis revealed the presence of ZnCl_2 . This shows that the method is not advisable due to selective volatility of Zn^{2+} in the presence of Cl^- ions at high-temperature stages of heat treatment, which modifies the composition.

The second method tested was the nitrate variant using nitrate salts. Calcium nitrate $\text{Ca}(\text{NO}_3)_2$ was prepared by dissolving calcium carbonate in nitric acid HNO_3 , since $\text{Ca}(\text{NO}_3)_2$ is very hygroscopic and difficult to dehydrate. TEOS was the source of SiO_2 .

It is known [8] that barium-bearing nitrate solutions are prone to sedimentation. If barium nitrate solution is poured into hydrolyzed ether of orthosilicic acid, a precipitate is formed immediately. To avoid the precipitation from the solution, it is necessary to thoroughly perform the dissolution and mixing of the components, after which barium nitrate should be poured into a mixture of the hydrolyzate (aqueous-alcohol TEOS solution) and solutions of aluminum, calcium, and zinc nitrates. Solutions of different components should be dispensed in small portions with intense stirring.

The gelation lasted approximately 2 days, which is presumably related to a large amount of water due to the low solubility of $\text{Ba}(\text{NO}_3)_2$.

We also implemented a third variant using acetates of metals that form part of the glass. In principle, SiO_2 can be introduced via silicon acetate, but in view of its high cost and scarce availability we used TEOS.

Gelation is registered already in 4 h, presumably due to the aggregation of hydrosol $\text{Al}(\text{OH})_3 \cdot x(\text{H}_2\text{O})$, which is inevitably formed in hydrolysis of $\text{Al}(\text{CH}_3\text{COO})_3$, on colloid particles. Aluminum acetate is very unstable and difficult to handle. The gel drying process has to be performed very carefully selecting appropriate time-temperature parameters, due to the high propensity of this material to coking.

The fourth variant was forming gel from a mixed solution that contained both nitrates and acetates of salts comprising the glass.

We slowly poured TEOS into a solution containing aluminum nitrate and zinc acetate (composition 1) under constant mixing; on doing so we observed a stratification of fluids. It was possible to achieve a homogenous solution by

adding ethyl alcohol under 30 min mixing due to the process of hydrolysis. Then a mixed solution of acetates was slowly poured into the mixture that was mixed for 60 min. A homogenous viscous sol was formed. Gel is formed after exposure for 4 h in a thermostat at 60–70°C.

This variant can be slightly modified by replacing zinc acetate by zinc nitrate. In this case the amount of water introduced decreases from 285 to 257 g, i.e., by 28 g per 100 g of the mixture (composition 2).

A comparison of the second variant using nitrates with the fourth variant using mixed solutions 1 and 2 shows that the required quantity of ethyl alcohol in the latter case is significantly lower and the difference amounts to 214 ml/100 g of the dry batch. The amount of water decreases by 33 ml per 100 g mixture for composition 1 or by 5 ml per 100 g mixture for composition 2.

The decrease in the amount of the organic component and water has a favorable effect on gel drying, heat treatment of xerogel, and clarification of the glass melt.

We investigated the dependence of the EPR spectra on the reactants introducing the required quantities of the glass components. The gel was a continuous material of diameter 2 mm and thickness 4 mm. It was transparent with a greenish shade. After drying, the sample was split into several parts and each segment was subjected to thermal treatment for 1 h in the range of 300–1500°C with an interval of 100°C. We investigated the dependence of EPR on the degree of milling of samples after drying and before thermal treatment.

The solutions were analyzed at 77 K (the liquid nitrogen temperature). The EPR spectrum in this case is a superposition of two spectra whose SFSs have different parameters, which points to the presence of two types of environment of the Cu^{2+} ion in the solution. Computer simulation of these spectra shows that one of them has the parameters $A_{\parallel} = 148 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\parallel} = 2.065$. The other spectrum has the parameters $A_{\parallel} = 140 \times 10^{-4} \text{ cm}^{-1}$, $g_{\parallel} = 2.306$, and $g_{\perp} = 2.056$. Since the values of these parameters are similar to those observed in frozen solutions, it can be inferred that Cu^{2+} in this sol exists in extended octahedrons of two types that presumably differ in the composition of their solvate shell. This is not surprising considering the complex composition of the liquid component of the solution. The second spectrum belongs to Cu^{2+} surrounded by water, since its parameters correspond to published data for frozen aqueous copper solutions, i.e., the copper complex constitutes an extended octahedron surrounded by six water molecules (hydrated complex).

Fresh gel at room temperature has a single spectrum with parameters $A_{\parallel} = 140 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\parallel} = 2.308$. The SFS in the perpendicular orientation is not resolved and $g_{\perp} = 2.055$ (Fig. 1). Similar spectra with virtually identical parameters are registered in dried gel and in samples heat-treated at 300–500°C. The similarity of these spectra suggests that water does not completely evaporate from the

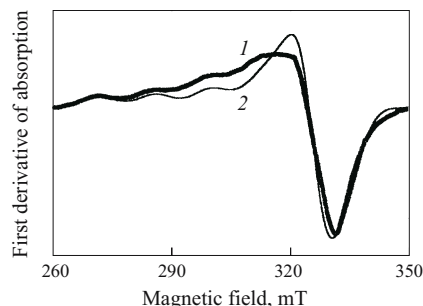


Fig. 1. Experimental (1) and calculated (2) EPR spectra of Cu^{2+} gel before drying.

pores of the sample in this temperature interval; accordingly, the ion Cu^{2+} , similarly to sol, is surrounded by water.

The spectrum dramatically changes its shape at 600 and 700°C (Fig. 2). Computer modeling shows that each spectrum consists of two spectra; one of them has a SFS with the same parameters as those indicated above, whereas the second one is a structureless isotropic line with g of the order of 2.1. The spectrum with the STF here as well belongs to the Cu^{2+} ions surrounded by water, which is not fully evaporated from the pores even at so high a treatment temperature. The structureless isotropic line corresponds to Cu^{2+} ions linked by spin-spin relations, i.e., at these temperatures copper tends to form clusters in certain parts of the samples, which is presumably related to the polycondensation of gel.

At 800°C, along with the hydrated copper spectrum we identified a low-intensity spectrum with a SFS and the parameters $A_{\parallel} = 153 \times 10^{-4} \text{ cm}^{-1}$, $g_{\parallel} = 2.37$, and $g_{\perp} = 2.045$, which are close to those observed in silicate glasses [9].

As the heat treatment temperature increases, the intensity of the signal related to glass formation grows and at 1300°C this signal exceeds the signal from the hydrated copper. However, water is present even at the temperature of 1500°C.

Figure 3 shows the ratio between the EPR signal from the hydrated copper and the signal from the vitreous phase. It can be seen that at 1500°C this ratio is equal to 30% for the case where the glass components are introduced via nitrates.

In using nitrate reactants, we observed wide STS lines which are the summation of the hydrated copper and the vitreous phase signals in approximate equal ratios, whereas the SFS lines for mixed reactants are narrower with the vitreous phase signal prevailing. The contribution of hydrated copper in the case of mixed reactants is lower than in the case of nitrate reactants, and at 1400–1500°C it is equal to 1–3%.

We have carried out experiments with nitrate reactants ground in a mortar after gel drying. After treatment at a temperature below 800°C the EPR spectra generally resemble those observed in the samples produced from granulated nitrates, i.e., they have spectra of hydrated copper. At 800°C we see a spectrum that differs qualitatively from the spectrum of the samples produced from granulated reactants.

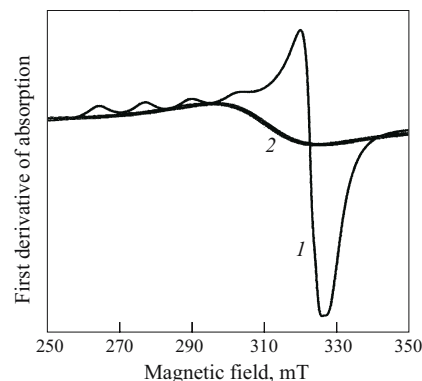


Fig. 2. EPR spectrum of Cu^{2+} in dried gel heat-treated at 700°C: 1) spectrum with SFS; 2) isotropic spectrum belonging to copper clusters.

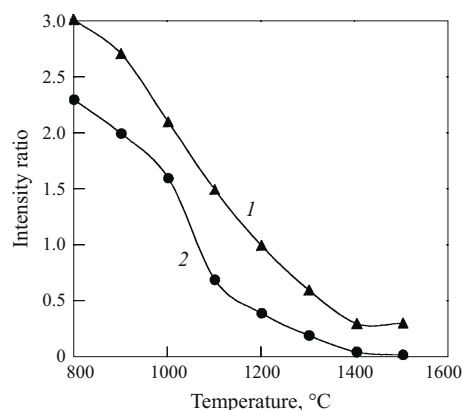


Fig. 3. Dependence of the ratio between the absorption signal from hydrated copper to the signal from the vitreous phase: 1) for reactants introduced via nitrates; 2) for reactants introduced via nitrates and acetates.

Such form with certain modifications persists up to a temperature of 1100°C. It is determined by the formation of copper clusters, which we attribute to the polycondensation of gel. This process in samples from milled nitrate reactants occurs at higher temperatures and is accompanied by a more heterogeneous distribution of copper. At temperatures of 1300–1500°C we see a SFS, but the main contribution is made by the hydrated copper ions. This contribution exceeds several times the signal from the vitreous phase.

Analysis of EPR spectra established the following:

- two types of Cu^{2+} centers coexist in solutions; one of them is solvated by the components introduced into the solution to produce glass, the other is solvated only by one of these components, namely water (hydrated copper);
- water persists in the glass pores up to the maximum heat treatment temperature;
- the content of water is significantly higher in the case where the glass-forming reactants are introduced via nitrates and sharply decreases using mixed nitrate-acetate reactants;

- the grinding of dried gel increases the content of hydrated copper;
- approximately after 800°C a vitreous phase of a preset composition starts to be formed in the samples;
- samples produced from mixed reactants and heat-treated at 1500 contain approximately 100% glass of a preset compositions and not more than 1% water.

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